Organic & Biomolecular Chemistry

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2019, **17**, 3741

Received 27th February 2019,
Accepted 22nd March 2019

DOI: 10.1039/c9ob00486f

rsc.li/obc

Radical fluoroalkylation reactions of (hetero) arenes and sulfides under red light photocatalysis†

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Fluoroalkylation reactions of (hetero)aromatics have been accomplished through the low-power illumination from red LEDs (λ_{max} = 635 nm) of commercially available perfluoroalkyl iodides R_F-I and phthalocyanine zinc salt as photocatalyst in MeCN : DMF solvent mixture. This methodology has been extended to the perfluorobutylation of sulfides. As far as we are concerned, this is the first report on a perfluoroalkylation reaction of (hetero)aromatics and sulfides under red-light photocatalysis.

Methodologies for fluoroalkylation reactions of organic compounds have come to the forefront within the organic chemist repertoire, especially those involving radicals.[1] Due to the electrophilic nature of perfluoroalkyl radicals R_F, electron-rich (hetero)aromatic cores along with high electron-density centers are excellent reacting partners.

Perfluoroalkyl radicals can be generated through direct visible light-induced homolysis of the perfluoroalkyl-iodides R_F-I bonds (*ca.* 201 kJ mol^{-1}, 590 nm), albeit, in poor yields. However, visible light irradiation of Electron Donor Acceptor (EDA) complexes formed between of R_F-I and nitrogen bases[2] or the halogen-bonding interactions from R_F-I with other heteroatom lone electron pairs (such as from sulfur or oxygen)[3] can lead to the production of R_F radicals in very efficient ways, thus overriding the low yields of R_F radicals obtained through direct visible light irradiation of R_F-I.[2]

Since the past decade, visible light-photocatalysis has represented a convenient way to generate radicals, especially since the advent of photocatalysts with convenient redox potentials (either reduction or oxidation potentials from organic dyes or organometallic photocatalysts) and the onset of inexpensive diodes as visible light sources.[4]

In the realm of photocatalysis, photocatalytic fluoroalkylation reactions have been the subject of renewed studies and interests.[5]

Eosin Y[6] or Methylene Blue[7] have also started to be investigated as organic photoredox catalysts under blue to green light irradiation (λ = *ca.* 450–550 nm). Through visible light-induced (white light) organic-dye photocatalysis, our group has studied the perfluoroalkykation reactions of aromatic amines,[8] thiols,[9] and heteroaromatic-*N*-oxides.[10]

Polypyridyl metal complexes such as Ir(ppy)$_3$ and Ru(bpy)$_3$ are key catalysts in this event, and blue- or white-light irradiation (λ = 375–450 nm) is required for the chemical transformations.[11] However, lower energy/power irradiation sources for photocatalysis have sparingly been explored.[12] Specially, photocatalysis under red light-irradiation to generate R_F radicals has only recently been disclosed by the group of Shibata and colleagues to accomplish perfluoroalkylation of olefins and alkynes with a synthetic trifluoroethoxy-coated boron sub-phthalocyanine.[13a]

We herein present the first preliminary results for the red light-induced commercially-available zinc-phthalocyanine-photocatalyzed fluoroalkylation reactions of diverse families of organic substrates such as (hetero)aromatics and thiol derivatives, demonstrating that combining low power red-light irradiation sources and a commercially available photocatalyst can bring about perfluoroalkylation of organic substrates efficiently. The use of red light as a low energy source and the appropriate photocatalyst can be regarded as a further stage of development for the production of R_F radicals and as an all-green process.

The isoindole moiety linked by nitrogen atoms in an array of four units is of special interest as the 18-π electron planar system shows extensive delocalization lending itself to applications as dyes and pigments.[14]

Phthalocyanines are promising dyes to be employed in red light-driven photocatalysis, due to their absorption bands at around 600–700 nm,[15] as well as subphthalocyanines which absorb nearby at 500–600 nm.[16] However, the poor solubility of these compounds limits their utility in organic reactions.[17]

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ob00486f

Intrigued by the results of Shibata and colleagues[13] on the perfluoroalkylation of olefins and alkynes under red light-irradiation with synthetic trifluororethoxy-coated boron subphthalocyanine[13a] and the perfluoroalkylation reactions of alkenes and alkynes under visible light irradiation with trifluororethoxy-coated zinc subphthalocyanine[13b] as photocatalysts, we commenced our studies by addressing solubility issues and seeking photocatalysts bearing convenient solubility in organic solvents with sufficient extinction coefficient at the irradiation wavelengths (λ = 635 nm) pertinent for the use of red LEDs.

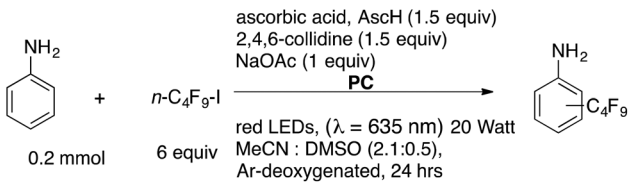
We first investigated the perfluoroalkylation of aniline with *n*-C_4F_9I by using various commercially-available photocatalysts under red light irradiation (Table 1, entries 1–3). We chose to include an amount of sodium L-ascorbate (as a mixture of ascorbic acid and 2,4,6-collidine/sodium acetate) as the initial reductant according to the work of Stephenson and co-workers, in an Ar-deoxygenated mixture of MeCN : DMSO (2.1 : 0.5) as solvent system.[18] Apparently, in the red light-driven system, powerful photocatalysts such as Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6, Eosin Y, and Methylene Blue completely failed to provide any perfluoroalkylation products (entries 1–3, Table 1). The former two PC (*i.e.*: Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 and Eosin Y) have very low extinction coefficients at the red-LEDs irradiation wavelength (λ = 635 nm).

We focused our attention to non-metallic 29*H*,31*H*-phthalocyanine **1** (Fig. 1) as PC, whose extended planar conjugated π-system absorbs in the red region of the electromagnetic spectrum (λ_{max} = 689 nm in THF). Constrained by the low solubility of **1** in MeCN or MeCN in admixtures with DMF or DMSO, we carried out the photocatalyzed reaction in THF as solvent. However, a low product yield was obtained (30% yield of combined 2-, and 4-perfluorobutylaniline, entry 4, Table 1). Addition of $Zn(OAc)_2$ led to a dramatic decrease in product yield (entry 5, Table 1).

1, 29H,31H-Phthalocyanine **2,** phthalocyanine Zn salt **3,** SAd = thioadamantyl

Fig. 1 Structures of 29*H*,31*H*-phthalocyanine **1**, phthalocyanine Zn salt **2**, and thioadamantyl-substituted Zn-phthalocyanine **3**.

Table 1 Optimization of the reaction conditions under red-light illumination from red LEDs (λ_{max} = 635 nm)



Entry	PC, (mol%)	AscH, eq.	Collidine, eq.	NaAc, eq.	Solv.	Yield,[a] %
1	Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6, (1)	1.5	1.5	—	MeCN DMSO	—
2	Eosin Y, (0.2)	1.5	1.5	—	MeCN DMSO	—
3	Methylene Blue, (0.2)	1.5	1.5	—	MeCN DMSO	—
4	1, (0.36)[c]	1.5	1.5	—	THF	30
5	1, (0.36)[b,c]	1.5	1.5	—	THF	—
6	3, (0.2)[d]	1.5	1.5	1	MeCN DMSO	57
7	3, (0.36)	1.5	1.5	1	MeCN DMSO	12
8	3, (0.36)	1.5	1.5	—	MeCN DMSO	90[e]
9	3, (0.36)	1.5	—	1	MeCN DMSO	38[f]
10	3, (0.36)	—	1.5	1	MeCN DMSO	—
11	3, (0.2)	1.5	—	—	MeCN DMSO	13
12	2, (0.36)[g]	1.5	1.5	—	MeCN DMF	93[h]

[a] ^{19}F NMR and ^{1}H NMR yields (benzotrifluoride as internal standard) of combined 2-perfluorobutylaniline 4-perfluorobutylaniline (and minor amounts of 2,4-bisperfluorobutyl-aniline) in a ratio *ca.* 0.4 : 1. [b] Addition of $Zn(OAc)_2$, 2 mg. [c] Reaction carried out in THF as solvent, 2,5 mL. [d] Photobleaching was observed after 24-hour irradiation with 0.01 equiv. of 3. [e] Remaining substrate: 9.5%. Ratio of 4 : 2 : 2,4-disubstituted products = 1 : 0.18 : 0.04. [f] Ratio of 4- : 2- : 2,4-disubstituted products = 1 : 0.26 : 0. [g] In MeCN : DMF (1 : 1) as solvent mixture. [h] 4- : 2-Isomer ratio = 1 : 0.4. Reaction carried out with 3 equiv. of *n*-C_4F_9-I.

Shibata and colleagues[13a] had attempted the trifluoromethylation of olefins and alkynes under red light irradiation employing the zinc salt of phthalocyanine (*i.e.*: **2**, Fig. 1, (λ_{max} = 674 nm in DMSO) in MeCN/MeOH as solvent mixture. However, no trifluoromethylation was obtained probably due to solubility problems.

Given the unsuccessful precedent reported by the authors[13a] when employing **2** as photocatalyst under red light, we chose to synthesize compound **3**, *i.e.*: 2,9(10),16(17),23(24)-tetrakis-(1-adamantylsulfanyl) phthalocyaninatozinc(II)[19] (Fig. 1) and explored its behavior as photocatalyst. We surmised that the thioadamantyl groups attached on the isoindole units would be beneficial in order to overcome solubility/aggregation issues associated with most phthalocyanines in organic solvents.

Photocatalyst **3** has a maximum absorption wavelength at 680 nm (λ_{max} emission = 687 nm, in THF), and the synthesis and spectroscopic properties have been described by one of us in previous reports.[19] The UV spectra of **1–3** along with the overlaid red-light LED emissive UV spectrum are shown in Fig. S1–S3.† In order to adjust or control irradiation times we investigated the photostability of **3** under continuous red-light irradiation (Fig. S4†) and found that **3** is sufficiently stable to undergo continuous irradiation under red light.

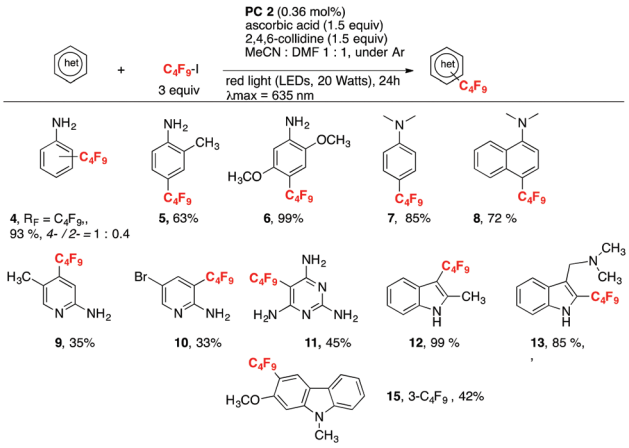
Knowing the well-suited photostability and spectroscopic properties of **3** we sought to optimize reaction conditions with this PC, according to Table 1. The combination of ascorbic acid, 2,4,6-collidine and PC **3** in MeCN : DMSO as solvent mixture enabled the perfluorobutylation of aniline in 90% yield according to conditions reported in Table 1 (entry 8).

Encouraged by the results with synthetic photocatalyst **3** in the solvent mixture MeCN : DMSO (2.1 : 0.5) we decided to revisit the use of commercially-available **2** (whose spectroscopic, redox, and stability properties are well known, Table S3†) in another solvent mixture unexplored by the previous report.[13a] To our delight, the perfluorobutylation reaction of aniline in the presence of ascorbic acid/2,4,6-collidine in MeCN : DMF solvent mixture (1 : 1) with PC **2** under red-light irradiation (λ_{max} = 635 nm) afforded 93% yield of combined 2-, and 4-perfluorobutylaniline (0.4 : 1 isomer ratio) (Table 1, entry 12).

With the optimized reaction conditions in hand, we decided to explore the perfluorobutylation reaction of a series of (hetero)aromatic compounds employing this time PC **2** in MeCN : DMF solvent mixture according to Scheme 1.

Red light-irradiation of aniline in the presence *n*-C_4F_9-I and PC **2** according to reaction conditions from Scheme 1 afforded a mixture of 2-/4-perfluorobutyl-substituted anilines **4** in 93% combined yield (2-/4-substituted ratio = 0.4 : 1).[8] The reaction of 2-methylaniline afforded only product **5** in 63% yield, while the reaction of 2,5-dimethoxyaniline gives product **6** quantitatively. The red-light-photocatalyzed reaction of *N*,*N*-dimethylaniline in the presence of *n*-C_4F_9-I gave only 4-perfluorobutyl-*N*,*N*-dimethylaniline **7** (Scheme 1) in 85% yield.[8]

The red light-photocatalyzed reaction of *N*,*N*-dimethyl-α-naphthylamine with *n*-C_4F_9-I afforded exclusively 4-perfluorobutyl-*N*,*N*-dimethyl-α-naphthylamine **8** in 72% yield



Scheme 1 Scope of the red-light (λ_{max} = 635 nm) photocatalyzed perfluoroalkylation of (hetero)aromatics (0.2 mmol) employing PC **2** (0.36 mol%). Yields represent isolated mass yields.

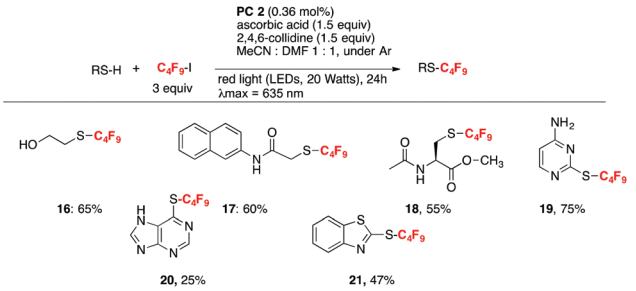
(Scheme 1). For comparison, the photoreaction of α-*N*,*N*-dimethyl-α-naphthylamine in the presence of *n*-C_4F_9-I under low-wavelength 350 nm irradiation[20] was reported to afford 4-perfluorobutyl-*N*,*N*-dimethylnapthylamine **8** in 57% yield. 2-Amino-5-methylpyridine, under reaction conditions of Scheme 1 affords 35% yield of **9**, while 2-amino-5-bromopyridine gives product **10** in 33% yield. 2,4,6-Triaminopyrimidine affords product **11** in 45% yield.

The red light-photocatalyzed reaction of 2-methylindole with *n*-C_4F_9-I afforded product **12** in 99% yield (Scheme 1). For comparison, the white LED-Eosin Y-photocatalyzed perfluorobutylation of 2-methylindole[21] was reported to give 84% yield of 3-perfluorobutyl-2-methylindole; however this latter yield was obtained under continuous flow white-light-irradiation. The red light-photocatalyzed reaction of natural product gramine (3-(dimethylaminomethyl)indole) with *n*-C_4F_9-I afforded product **13** in 85% (Scheme 1). 2-Methoxy-9-methylcarbazole **14** affords 47% yield of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15**, and minor amounts (≤5%) of another isomer of formula $C_{18}H_{12}F_9NO$ that could not be isolated from the reaction mixture.

Radical photocatalytic perfluoroalkylation of sulfides has been pursued with $Ru(bpy)_3Cl_2$ as photocatalyst[22] under white light irradiation (CFL), or through visible-light-photoexcited EDA complexes,[9] among the most recent environmentally-benign radical-based strategies.

We decided to extend our all-green red-light photocatalytic protocol to explore the perfluorobutylation of sulfides. The scope of the red-light photocatalyzed (PC **2**) perfluorobutylation of sulfides is illustrated in Scheme 2.

The reaction of β-mercaptoethanol with *n*-C_4F_9-I in the presence of ascorbic acid, 2,4,6-collidine in Ar-deoxygenated MeCN : DMF solvent mixture (1 : 1) under red-light irradiation (red LEDs, λ = 635 nm, 20 Watt, 24 h) with PC **2** afforded product **16** in 65% yield (Scheme 2). For comparison, the white-light electron-photocatalyzed[9] reaction of

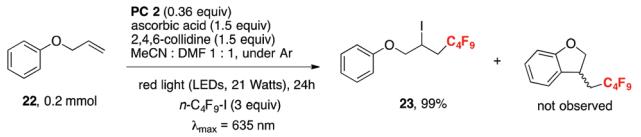


Scheme 2 Scope of the red-light (λ_{max} = 635 nm) photocatalyzed perfluoroalkylation of sulfides (0.2 mmol) employing PC **2** (0.36 mol%). Yields represent isolated mass yields.

β-mercaptoethanol afforded 75% of product **16**. 2-Mercapto-*N*-(naphthalen-2-yl)acetamide under the same reaction conditions afforded *N*-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17** in 60% yield (Scheme 2). The red light-induced reaction of the amino acid derivative *N*-acetyl cysteine-methylester (the methyl ester of *N*-acetylcysteine, NAC, which is used to treat paracetamol (acetaminophen) overdose, and in individuals with cystic fibrosis or chronic obstructive pulmonary disease), gave product **18** in 55% yield (Scheme 2). In contrast, the 24 Watt CFL – electron-photocatalyzed reaction of analogous methyl (butoxycarbonyl) cysteinate was reported to afford 50% yield of methyl *N*-(*tert*-butoxycarbonyl)-*S*-(perfluorobutyl)-L-cysteinate,[9] whereas the white-light $Ru(bpy)_3Cl_2$-photocatalyzed reaction of analogous methyl (butoxycarbonyl)cysteinate, afforded 85% yield of *N*-(*tert*-butoxycarbonyl)-*S*-(perfluorobutyl)-L-cysteinate.[22] Reaction of 4-amino-2-mercaptopyrimidine gave product **19** in 75% yield (Scheme 2). For comparison, the electron-catalysed perfluorobutylation of 4-amino-2-mercaptopyrimidine was reported to afford product **19** in 48% yield, in a mixture of DMSO : DMF as solvent.[9] 6-Mercaptopurine (Purinethol©, a medication used to treat cancer and autoimmune diseases) afforded product **20** in 25% yield. 2-Mercaptobenzothiazole afforded product **21** in 47% yield. These comparisons show that the red-light driven photocatalyzed protocol affords better yields than the electron-catalyzed (EDA) method[9] (for substrates **18** and **19**), and better or comparable yields with those obtained with Eosin Y[21] (substrate **12**) and the Rose-Bengal-photocatalyzed reactions[8] (substrates **4**, **7**, **16**).

The reaction seems to proceed through radicals, as revealed by experiments performed in the presence of radical scavengers such as TEMPO (entry 1, Table S2†), where entire suppression of product is observed. The presence of 1,4-dinitrobenzene, a well-known radical anion scavenger, affords a notorious decrease in the perfluorobutylation of aniline (30% product yield, entry 2, Table S2†).

The red-light-photocatalyzed (PC **2**) reaction of (allyloxy) benzene **22** in the presence of *n*-C_4F_9-I affords the ATRA (atom transfer radical addition) product ((7,7,7,7,7,7,7,7,7-nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **23** quantitatively, according to Scheme 3. No intramolecular cyclization

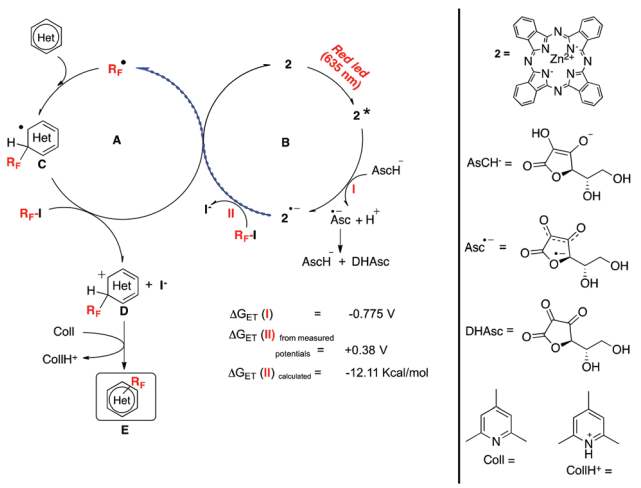


Scheme 3 Red-light-photocatalyzed reaction of allyloxybenzene **22**.

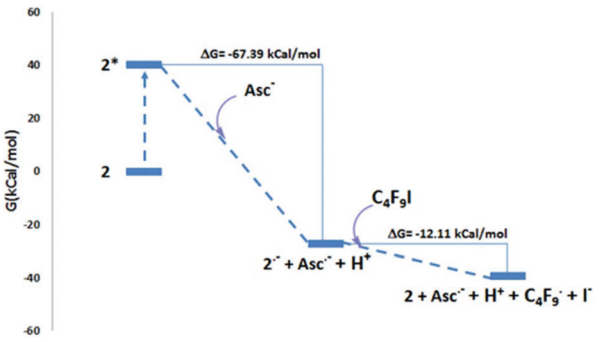
product was obtained, purporting that the ATRA reaction is faster than the intramolecular cyclization of the phenylallyloxyl-perfluorobutyl-substituted radical.

Surprisingly the reaction in the presence of oxygen, affords only a slight decrease in product yield (entry 3, Table S2†). The reaction in the absence of illumination (dark reaction, entry 4, Table S2†) does not afford product, whereas the reaction carried out with PC **2** under white light illumination (entry 5, Table S2†) led to 30% yield of substitution product, probably from white-light-induced homolysis of C_4F_9-I bond. The reaction under red light irradiation in the absence of PC **2** (entry 6 Table S2†) afforded less than 5% yield of substitution product. These results indicate that excitation of PC **2** under red-light is required for substitution to proceed.

A plausible reaction mechanism is proposed involving cycles **A** and **B** (Scheme 4). Initially, red-light-photoexcited phthalocyanine zinc salt **2** accepts one electron from collidinium ascorbate[23a] (the salt formed from ascorbic acid and 2,4,6-collidine) to form the anion radical of **2**$^{\bullet}$—(supported by the Stern Volmer results, Fig. S5,† where quenching of the fluorescence of **2*** was obtained in the presence of ascorbic acid/collidine) along with formation of ascorbate radical anion Asc$^{\bullet}$—, and concomitant loss of H^+ and one electron.[23b,c] This process (**I**, Scheme 4) has a favourable Gibbs energy (ΔG_{ET} = −0.775 V, see Table S3† for determination) and a highly exothermic calculated ΔG = −67.39 kcal mol^{-1} (see ESI, section VI,† for theoretical calculations, and Scheme 5).[24,25a] The anion radical of **2**$^{\bullet-}$ (E_{red} = −0.89 V *vs.* SCE[26]) should



Scheme 4 Proposed reaction mechanism for the red-light photocatalyzed perfluoroalkylation of (hetero)arenes.



Scheme 5 Free energies (kcal mol^{-1}) of the reductive photoredox cycle of photoexcited Zn-phthalocyanine **2*** with ascorbate anion to produce the radical anion of **2**$^{\bullet-}$, ascorbate radical anion and proton.

reduce C_4F_9I (E'_{red} = −1.27 V *vs.* SCE)[21] to generate the C_4F_9 radical. Although this reduction process (**II**, Scheme 4) is a thermodynamically unfavorable electron transfer[25b] from the reduced photocatalyst to C_4F_9I (about +0.38 V, see Table S3†), collidinium ascorbate presumably acts as a Lewis acid to support this step through the activation of the carbon iodine (C–I) bond to overcome this endergonic event. This suggestion is partially supported by the result reported by Stephenson and co-workers.[25c,d] Also, Shibata and colleagues[13a] in the sub-phthalocyanine-photocatalyzed trifluoromethylation of olefins under red light determine an endergonic ΔG_{ET} process by more than +0.5 V, from the excited photocatalyst to CF_3-I; the reduction of the CF_3-I by PC* still taking place.[13a] As a matter of fact, the R_F-I bond has been shown to be weakened under photoinitiation in the presence of chloride ions,[27] amines,[28] and carbonyl compounds (esters).[29] However, our theoretical calculations (*vide infra* Scheme 5, and section VI, ESI†) reveal that ΔG from the excited PC **2*** to C_4F_9I is indeed an exergonic process with a value of −12.11 kcal mol^{-1}. The ET-reduction of C_4F_9I by Asc$^{\bullet}$—could further be proposed to produce R_F radicals; however this process has a more unfavourable ΔG_{ET} (for ΔG_{ET} see Table S3, Scheme S5†). Propagation of the chain by ET between Asc$^{\bullet}$—and PC **2** is precluded as the fate of Asc$^{\bullet}$—is likely to be disproportionation to dehydroascorbic acid and ascorbate monoanion and therefore Asc$^{\bullet}$—cannot be proposed to act as a chain carrier.[30] The C_4F_9 radical species adds to the (hetero)aromatic compound (cycle **A**, Scheme 4) to produce intermediate **C** which has enough reductive potential[31] to undergo facile oxidation to a Wheland intermediate **D** by C_4F_9-I and to follow cycle **A**. The presence of base (2,4,6-collidine) warrants proton abstraction from the Wheland intermediate **D** to yield the perfluoroalkylated(hetero)aromatic compound **E**. Theoretical calculations for cycle **A** Scheme 4 can be found in ESI.† Further mechanistic studies are underway.

Conclusions

Preliminary results from homolytic (hetero)aromatic substitutions of (hetero)arenes with C_4F_9 radicals have been accomplished under the low-power red-light irradiation (red LEDs, λ = 635 nm) employing commercial zinc-phthalocyanine **2** as photocatalyst in MeCN : DMF solvent mixture. As far as we are concerned, this is the first report on a perfluoroalkylation reaction of (hetero)aromatics and sulfides under red-light photocatalysis. The use of PC **2** in a red-light-driven process for the perfluoroalkylation reaction of (hetero)aromatics and sulfides represents a friendlier environmental alternative when compared with visible-or blue-light driven Rose Bengal, Eosin Y, or $Ru(bpy)_3Cl_2{\cdot}6H_2O$ photocatalysts. The current methodology could also be advantageous when employing substrates absorbing in the visible region of the spectrum. To that effect, we are currently investigating the perfluoroalkylation reactions of substrates absorbing in the 450–550 nm range, where conventional visible-light photocatalysts cannot be used. As for the perfluorobutylation of sulfides, the red-light methodology results in efficient perfluoroalkyl thio ethers in good yields. We are currently studying the reaction mechanism for radical perfluoroalkyaltion of sulfides under red light.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 S. Barata-Vallejo, M. Victoria Cooke and A. Postigo, *ACS Catal.*, 2018, **8**, 7287–7307.
2 A. Postigo, *Eur. J. Org. Chem.*, 2018, 6391–6404.
3 Y. Wang, J. Wang, G.-X. Li, G. He and G. Chen, *Org. Lett.*, 2017, **19**, 1442–1445.
4 (*a*) L. Marzo, S. K. Pagire, O. Reiser and B. König, *Angew. Chem., Int. Ed.*, 2018, **57**, 10034–10072; (*b*) J. J. Douglas, M. J. Sevrin and C. R. J. Stephenson, *Org. Process Res. Dev.*, 2016, **20**, 1134–1147.
5 (*a*) S. Barata-Vallejo, S. M. Bonesi and A. Postigo, *Org. Biomol. Chem.*, 2015, **13**, 11153–11183; (*b*) T. Chatterjee, N. Iqbal, Y. You and E. J. Cho, *Acc. Chem. Res.*, 2016, **49**, 2284–2294; (*c*) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160–4163; (*d*) T. Rawner, E. Lutsker, C. A. Kaiser and O. Reiser, *ACS Catal.*, 2018, **8**, 3950–3956; (*e*) R. Beniazza, L. Remisse, D. Jardel, D. Lastécouères and J.-M. Vincent, *Chem. Commun.*, 2018, **54**, 7451–7454; (*f*) G. Magagnano, A. Gualandi, M. Marchini, L. Mengozzi, P. Ceroni and P. G. Cozzi, *Chem. Commun.*, 2017, **53**, 1591–1594; (*g*) E. Arceo, E. Montroni and P. Melchiorre, *Angew. Chem., Int. Ed.*, 2014, **53**, 12064–12068.
6 (*a*) N. J. W. Straathof, H. P. L. Gemoets, X. Wang, J. C. Schouten, V. Hessel and T. Noël, *ChemSusChem*, 2014, **7**, 1612–1617; (*b*) M. Neumann, S. Füldner, B. König and K. Zeitler, *Angew. Chem., Int. Ed.*, 2011, **50**, 951–954; (*c*) T. Yajima and M. Ikegami, *Eur. J. Org. Chem.*, 2017, 2126–2129.

7 S. P. Pitre, C. D. McTiernan, H. Ismaili and J. C. Scaiano, *ACS Catal.*, 2014, **4**, 2530–2535.
8 S. Barata-Vallejo, D. E. Yerien and A. Postigo, *Eur. J. Org. Chem.*, 2015, 7869–7875.
9 D. E. Yerien, S. Barata-Vallejo, B. Camps, A. E. Cristófalo, M. E. Cano, M. L. Uhrig and A. Postigo, *Catal. Sci. Technol.*, 2017, **7**, 2274–2282.
10 B. Lantaño, S. Barata-Vallejo and A. Postigo, *Org. Biomol. Chem.*, 2018, **16**, 6718–6727.
11 (*a*) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363; (*b*) M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926.
12 (*a*) R. Gerdes, L. Lapok, O. Tsaryova, D. Wöhrle and S. M. Gorun, *Dalton Trans.*, 2009, 1098–1100; (*b*) A. B. Sorokin, *Chem. Rev.*, 2013, **113**, 8152–8191.
13 (*a*) K. Matsuzaki, T. Hiromura, E. Tokunaga and N. Shibata, *ChemistryOpen*, 2017, **6**, 226–230; (*b*) K. Matsuzaki, T. Hiromura, H. Amii and N. Shibata, *Molecules*, 2017, **22**, 1130, DOI: 10.3390/molecules22071130.
14 (*a*) J. Mack and N. Kobayashi, *Chem. Rev.*, 2011, **111**, 281–321; (*b*) L. Martín-Gomis, F. Fernández-Lázaro and Á. Sastre-Santos, *J. Mater. Chem. A*, 2014, **2**, 15672–15682; (*c*) M. E. Ragoussi, I. Mine and T. Torres, *Eur. J. Org. Chem.*, 2013, 6475–6489.
15 (*a*) J. Mack and N. Kobayashi, *Chem. Rev.*, 2011, **111**, 281–321; (*b*) N. Kobayashi, N. Sasaki, Y. Higashi and T. Osa, *Inorg. Chem.*, 1995, **34**, 1636–1637; (*c*) N. Kobayashi, H. Ogata, N. Nonaka and E. A. Luk'yanets, *Chem. – Eur. J.*, 2003, **9**, 5123–5134.
16 (*a*) A. Studer, *Angew. Chem., Int. Ed.*, 2012, **51**, 8950–8958, (*Angew. Chem.*, 2012, **124**, 9082–9090); (*b*) E. Merino and C. Nevado, *Chem. Soc. Rev.*, 2014, **43**, 6598–6608; (*c*) E. J. Cho, *Chem. Rec.*, 2016, **16**, 47–63.
17 A. B. Sorokin, *Chem. Rev.*, 2013, **113**, 8152–8191.
18 C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875–8884.
19 N. C. López Zeballos, M. C. García Vior, J. Awruch and L. E. Dicelio, *J. Photochem. Photobiol., A*, 2012, **235**, 7–13.
20 S. Barata-Vallejo, M. Martín Flesia, B. Lantaño, J. E. Argüello, A. B. Peñéñory and A. Postigo, *Eur. J. Org. Chem.*, 2012, 998–1008.
21 N. J. W. Straathof, D. J. G. P. van Osch, A. Schouten, X. Wang, J. C. Schouten, V. Hessel and T. Noeel, *J. Flow Chem.*, 2014, **4**(1), 12–17.
22 C. Bottecchia, X.-J. Wei, K. P. L. Kuijpers, V. Hessel and T. Noeel, *J. Org. Chem.*, 2016, **81**, 7301–7307.
23 (*a*) T. Iyanagi, I. Yamazaki and K. F. Anan, *Biochim. Biophys. Acta*, 1985, **806**, 255–261; (*b*) J. J. Warren and J. M. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 7546; (*c*) J. J. Warren and J. M. Mayer, *J. Am. Chem. Soc.*, 2010, **132**, 7784.
24 M J. W. Taylor, W T. Eckenhoff and T Pintauer, *Dalton Trans.*, 2010, **39**, 11475–11482.
25 (*a*) *The Porphyrin Handbook: Phthalocyanines: Spectroscopic and Electrochemical*, ed. K. Kadish, R. Guilard and K. M. Smith, 2002, p. 152; (*b*) Thermodynamically unfavourable electron transfer process is also observed, see: Y. Shen, J. Cornella, F. Juliá-Hernández and R. Martin, *ACS Catal.*, 2017, **7**, 409–412; (*c*) C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875–8884; (*d*) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160–4163.
26 D. W. Clarck, N. S. Hush and I. S. Woolsey, *Inorg. Chim. Acta*, 1976, **19**, 129–132.
27 R. Beniazza, L. Remisse, D. Jardel, D. Lastécouère and J.-M. Vincent, *Chem. Commun.*, 2018, **54**, 7451.
28 Y. Wang, J. Wang, G.-X. Li, G. He and G. Chen, *Org. Lett.*, 2017, **19**, 1442.
29 L. Wozniak, G. Magagnano and P. Melchiorre, *Angew. Chem., Int. Ed.*, 2018, **57**, 1068.
30 G. A. Dilabio and J. S. Wright, *Free Radical Biol. Med.*, 2000, **29**, 480–485.
31 D. D. M. Wayner and A. Houmam, *Acta Chem. Scand.*, 1998, **52**, 377–384.

